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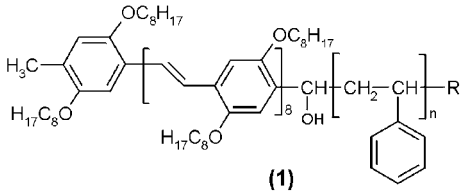
Microporous Honeycomb-Structured Films of Semiconducting Block Copolymers and Their Use as Patterned Templates**

By *Bert de Boer*, *Ulf Stalmach*, *Harry Nijland*, and *Georges Hadziioannou**

Block copolymers are known to microphase-separate giving rise to ordered structures with nanometer scale periodicity. Moreover, it was observed recently that rod–coil block copolymers and amphiphiles, when thin films are cast from appropriate solvents on solid substrates, spontaneously form highly ordered, micro-porous honeycomb structures with a characteristic length scale.[1–10] These films, with pore sizes in the order of micrometers, find applications in photonic[11] and opto-electronic devices,[12] catalysis, thermal insulation materials,[13] and membranes.[14] Usually, for the preparation of micro-porous materials, colloidal particles are used as templates, which have to be removed afterwards by solvent extraction or other tedious techniques.

We synthesized a series of rod–coil block copolymers by "living" free radical polymerization method using a derivative of 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO). We modified a mono-aldehyde-functionalized poly(2,5-dioctyloxy-*p*-phenylene vinylene) (rigid rod), prepared by a Siegrist polycondensation,[15] to its nitroxide-functionalized analogue, which was used subsequently as a macro-initiator in the (co)-polymerization of styrene and styrene derivatives[16] (coil block) (Scheme 1). Drop casting of solutions of these novel block copolymers from CS_2 and 1,2-dichloroethane resulted in the formation of honeycomb structures.



(1)

Scheme 1. $DOOPPV_{3.2k}$-*b*-PS_{12k} (**1**), where R represents the TEMPO end-group.

In this paper, we demonstrate the formation of this honeycomb structure by the light-emitting rod–coil block copolymer, poly(2,5-dioctyloxy-*p*-phenylene vinylene)-*b*-polystyrene ($DOOPPV_{3.2k}$-*b*-PS_{12k}), and the use of the highly ordered, micro-porous films as a template for patterned structures (e.g., aluminum).

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Upon drop casting a 0.1 wt.-% $DOOPPV_{3.2k}$-*b*-PS_{12k} (**1**)/CS_2 solution onto a glass slide in a flow-hood, we observed the condensation of water on the surface of the liquid film. After complete evaporation of the solvent, the samples were investigated by optical and fluorescence microscopy, revealing a highly ordered, two-dimensional hexagonal, close-packed air-hole structure in the polymer film, shown in Figure 1. In optical transmission, the bright spots correspond to the cavities, which transmit the light completely. The fluorescence microscopy reveals the honeycomb structure, indicating that the fluorescent block (DOOPPV) is homogeneously distributed in the solid film.

A top view of the film with scanning electron microscopy (SEM) clearly displays the open surface structure of the polymer film with hole diameters of 2–3 μm (Fig. 1). The SEM-imaging of the cross section of the free standing film revealed the presence of spherical cavities with a diameter of 3–5 μm (Fig. 1, inset).

The SEM images of the cross section also show that the cavities in the polymer film are mutually connected. However, it is not clear at the moment whether the mutual connections are created during the preparation of the film for SEM imaging, or whether their occurrence is an intrinsic phenomenon in the formation of the polymer film.

We believe that the cavity pattern originates from the presence of water droplets, which at some stage form a two-dimensional uniform array. The water condensation on the evaporating thin film of the polymer solution and the subsequent water droplet formation, due to surface instabilities like Rayleigh–Taylor or Marangoni, which constitutes the template for the honeycomb polymer film formation, is the result of the cooling of the film surface during the evaporation of carbon disulfide. During the evaporation process, the surface reaches a minimum temperature of –6 °C as measured with an infrared thermometer. When CS_2 has evaporated completely, the water droplets are immobilized in the polymer film. The sample then warms up, resulting in the expansion and subsequent evaporation of the encapsulated water droplets, after blistering the very thin top layer of the polymer film. This blistering process leaves behind a volcano-like structure at the polymer surface as was revealed with atomic force microscopy (AFM) imaging (Fig. 1).

By the vapor deposition method of metals or organics on the honeycomb polymer film (template), a very regular pattern of functional hexagonally ordered dots could be prepared. As the polymer film should be washed away after the deposition process, one is restricted to materials being insoluble in the same solvent as the templating polymer matrix.

In short, the processing steps in creating a regular pattern of e.g., aluminum are as follows. First, the honeycomb structure was exposed to blue light (475–495 nm) for 10 min, whereby only the exposed surface of the polymer matrix ($\lambda_{abs,max}$ = 470 nm) is photo-crosslinked. The photo-crosslinking is probably due to repeated photocyclodimerization of the vinyl bonds in the PPV-block.[17] During the exposure, we observed a change in fluorescence from yellow to green, indicating a

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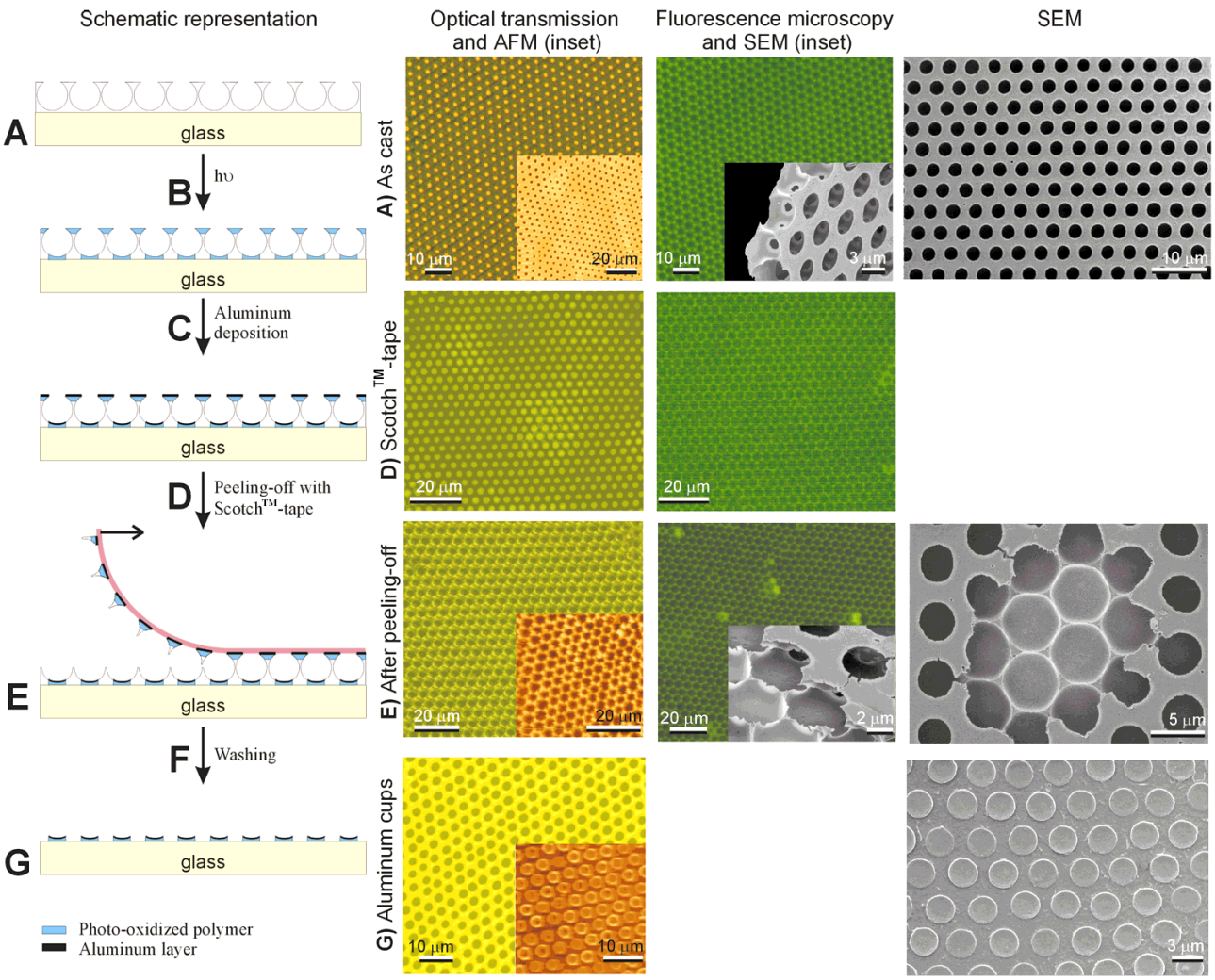

Fig. 1. Schematic representation, optical transmission microscopy, AFM, fluorescence microscopy, and SEM images of top view and free standing films (inset) after the processing steps in the preparation of aluminum cups on glass starting from a honeycomb-structured film: A) initial honeycomb structure, B) photo-oxidation of the exposed surface, C) deposition of aluminum, D) removal of the top layer with Scotch-tape, E) structure obtained after removing the aluminum-coated top layer, F) washing of unexposed polymer matrix with chloroform, and G) final structure of hexagonally packed aluminum cups.

decrease of the conjugation length. Subsequently, a 40 nm layer of aluminum was vapor-deposited onto the polymeric honeycomb structure. After removing the aluminum-coated top layer with Scotch-tape and washing away the unexposed polymer layer with chloroform, a hexagonally packed array of aluminum cups with a depth of ~160 nm remains on the surface (Fig. 1). The aluminum cups are bowl-like disks with a diameter of 3.5 μm and a height of 200 nm at the edges and 40 nm in the center of the cups. The shape of the cups is obviously due to the spherical shape of the cavities in the honeycomb structure. The process results in roughly 6.5×10^6 cups of aluminum per cm^2. It constitutes a rapid and easy method for preparing patterned electrodes or photolithography masks with relatively large features compared to modern techniques like e-beam lithography. Figure 1 displays a schematic representation, and optical transmission, fluorescence microscopy, AFM, and SEM images taken after each of the processing steps in the preparation of aluminum cups on a glass surface. Furthermore it displays the complementary optical transmission and fluorescence microscopy images of the Scotch-tape used in the peeling process.

In conclusion, we have described the formation of honeycomb structures by DOOPPV$_{3.2k}$-*b*-PS$_{12k}$. The morphology of the honeycomb structure was characterized by AFM, SEM, fluorescence and optical microscopy. It consists of a two-dimensional array of spherical cavities with a diameter of 3–5 μm in a polymer film. This polymer film has an open structure showing holes with a diameter of 2–3 μm at the surface. This open structure was subsequently used as a template for the formation of a two-dimensional hexagonal array of functional dots, e.g., aluminum cups.

Experimental

The synthesis of poly(2,5-dioctyloxy-*p*-phenylene vinylene)-*b*-polystyrene (**1**) or DOOPPV$_{3–5k}$-*b*-PS$_{5–25k}$ block copolymers by "living" radical polymerization is described elsewhere [16].

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Solutions of 0.1 wt.-% block copolymer in CS_2 were dropcast on cleaned substrates (glass slides, freshly cleaved mica for AFM, quartz, etc.) in a flow-hood. The surface temperature was measured with an Optex thermo-hunter HR-1 FS infrared thermometer at a distance of 10 cm. Optical transmission and fluorescence microscopy were performed on a Carl-Zeiss Axiophot microscope equipped with a high-resolution charge coupled device (CCD) camera (Sony DKC 5000), which was connected to a frame grabber and a personal computer for image processing. Prior to imaging by SEM, the samples were coated with 3 nm Pt/Pd (80/20). SEM images were recorded using a JEOL 6320F field emission microscope working at 2 kV and a beam current of 1×10^{-10} A. Free-standing films were obtained by ultrasonically agitating the cast film and collecting the floating film from the water surface. AFM images were recorded with a Topometrix Discoverer TMX 2010, mounted with Si_3N_4 tips. Topographic images were taken in air at a force of about 10 nN in contact mode.

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Inhomogeneous Photon Emission Properties of Self-Assembled Metallic Nanocrystals

By *Alexander O. Gusev*, *Abdelhafed Taleb*, *Fabien Silly*, *Fabrice Charra*, and *Marie-Paule Pileni**

Self-assembled nanocrystals and their specific properties represent an area between macroscopic and microscopic physics that has progressed rapidly over the last five years. It has been widely demonstrated that nanocrystals are able to self-assemble in two-dimensional (2D) hexagonal networks or in 3D face-centered cubic (FCC) "pseudo"-crystals.[1–3] Recently it has been shown that the physical properties of silver[4,5] and cobalt[6–8] nanocrystals organized in 2D and/or 3D superlattices differ from those of isolated nanocrystals. Collective properties are observed. Furthermore, the continuous miniaturization of microelectronics raises the prospect of exploiting the novel properties emerging at the nanometer scale.[9] This has motivated a considerable number of multidisciplinary studies on model nanometer-sized single-electron systems. Superlattices of ordered nanocrystals represent an exciting new class of materials and there is great interest in developing a fundamental understanding of their intrinsic properties.

Most experimental investigations in this domain rely on measurements of current–voltage characteristics. Scanning tunneling microscopy (STM) operating in both imaging and spectroscopic modes is an indispensable tool for exploring down to the atomic level. The STM tip offers another possibility: it can be used as an extremely localized source of low-energy electrons to locally excite photon emission from a variety of metal films. The detection of locally excited luminescence at the junction of a STM tip provides access to electron dynamic properties at the surface, which makes it possible to study luminescence phenomena of nanometer-sized structures. This provides local information on chemical,[10,11] electronic,[12,13] and optical[13–15] properties.

STM-induced photon emission from metal substrates has been identified as arising from radiative decay of plasmon modes[10,16,17] excited by inelastic electron tunneling (IET) from the biased tip to the surface and localized between them. The influence of surface morphology has been studied experimentally on rough granular surfaces.[13,15] It revealed the influence of local surface curvature on emission spectra and confirmed the role of plasmon modes. Emission from metal aggregates formed by vapor deposition on a conducting substrate showed a clear dependence of efficiency[18,19] and spectrum[20] on the aggregate size. Several optical plasmon modes can exist through the coupling of spherical-particle modes with each other and with substrate surface plasmons.[21]

In this paper, a correlation between photon maps and STM images is presented. There are large variations in photon-emission efficiency depending on how tightly the particle is embedded within its hexagonal network. This effect can be explained either in terms of interaction of hot electrons with the nanocrystals' surface phonon modes or as a local change in tip-particle voltage drop.

The synthesis of silver nanocrystals with 4 nm average diameter and coated with dodecanethiol has been extensively described elsewhere[3] and is reported in the experimental section. These nanocrystals were then dispersed in hexane. When a drop of the solution was deposited on an atomically flat gold(111) surface[22] and the solvent evaporated at room temperature, organized arrays of dodecanethiol-capped silver nanocrystals formed. The sample was introduced into a multichamber UHV-STM immediately after solvent evaporation. A quantitative Auger-electron spectrum analysis confirmed

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